On the influence of rare earth doping on microstructure and phase composition of sputtered, epitaxial Bi$_2$Sr$_2$(Ca$_{x-1}$RE$_x$)Cu$_2$O$_{8+\delta}$ films and multilayers

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Abstract

We report on the preparation and the structural analysis of Bi$_2$Sr$_2$(Ca$_{x-1}$RE$_x$)Cu$_2$O$_{8+\delta}$ (BSCRECO) thin films and multilayers. In-situ sputtered normal-conducting–superconducting (N–S) bilayers, dedicated as basic for coplanar high $T_c$ Josephson junctions, reveal almost perfect interfaces in high resolution transmission electron microscopy (HRTEM) analysis. A mechanism for stabilization of the crystallographic structure of superconducting BSCRECO thin films is proposed. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Efforts in high temperature superconducting (HTS) thin film fabrication are primarily defined by the requirements of superconductor electronics. High quality HTS thin films and multilayers are indispensable for the fabrication of integrated junction circuits. The most common HTS material of choice for this kind of applications is still Y$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ (YBCO). YBCO, however, suffers from a loss of oxygen and a fast degradation in air. Bismuth based superconductors, in contrast, are rather stable with respect to oxygen losses. In spite of the difficulties to deposit Bi$_2$Sr$_2$Ca$_{2}$Cu$_2$O$_{8+\delta}$ (BSCCO 2212 or just 2212 in the following), several laboratories managed to establish a technology for the reproducible fabrication of high quality BSCCO 2212 thin films [1–3]. Bi-based cuprates belong to the homologue series Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{2n+4+\delta}$ with specific transition temperatures $T_c$ ranging from $T_c = 20$ K (2201 phase), 85 K (2212 phase) and 110 K (2223 phase), for $n = 1, 2$ and 3, respectively [4]. The only difference between two consecutive phases is the addition of a double CaCuO$_2$ block in the perovskite subunit, increasing the $c$-axis parameter. The $a$- and $b$-axis parameters remain almost unchanged. The close vicinity of the three phases in the phase-diagram leads to a nonstoichiometric composition if the growth parameters are not chosen appropriately. If the difference of the free energies between two phases becomes too low, stacking faults will occur.

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According to high resolution transmission electron microscopy (HRTEM) investigations [5,6], DC sputtered 2212 films are usually not homogeneous with respect to their composition. They mainly consist of $\text{Bi}_x\text{Sr}_{y-1}\text{Ca}_n\text{Cu}_{2n+4+\delta}$ layers (or stacks of the latter) with $n = 2$ and $n = 3$, occasionally containing layers with $n = 4$ or $5$. The varying stacking sequences in different film regions result in a high density of stacking faults in the film. All these features are undesirable with respect to a well-defined, regular film structure essential for the fabrication of Josephson junctions. Our approach to solve this problem is a weak chemical doping by rare earth (RE) ions. RE doping in the BSCCO-system is well known to force a metal-insulator transition (MIT) [8]: The substitution of divalent Ca by RE ions, e.g., Y$^{3+}$ or Gd$^{3+}$ in $\text{Bi}_x\text{Sr}_{y-1}\text{Ca}_n\text{RE}_x\text{Cu}_{2n+4+\delta}$ reduces the amount of holelike carriers and leads to a MIT above a critical concentration. We apply RE doping both below and above this critical concentration.

The focus of this work is the utilization of the different impacts of this RE substitution with respect to the fabrication of high quality BSCCO films and multilayers for rapid single flux quantum (RSFQ) device applications. A doping-controlled MIT offers essential advantages for the fabrication of SNS junctions and circuits: Crystallographic continuity at the interface can be achieved and the barrier properties can be controlled by the degree of RE doping. Moreover, the stabilization of the BSCCO-2212 phase in superconducting films by an optimized weak doping is a step towards the reproducible fabrication of ion-implanted Josephson junctions, because the crystallographic quality plays an essential role in these devices.

2. Experimental and results

2.1. Deposition technique

BSCCO thin films and multilayers are deposited in a self-made multi-target DC on-axis sputtering system. The targets of different stoichiometry are prepared by an optimized solid-state reaction at temperatures between 860°C and 900°C, depending on the doping concentration. The high pressure planar DC sputtering system comprises a vacuum chamber with a water-cooled cathode mounted on top and a heated substrate holder at the bottom. The heater with the substrate is linearly movable between four targets, which enables the in-situ stacking of differently doped thin layers. The films were sputtered onto (100)-SrTiO$_3$ substrates under pure oxygen atmosphere. Their oxygen content was adjusted by controlling the flow and pressure of the oxygen sputtering atmosphere independently [1].

2.2. High-resolution transmission electron microscopy

Cross-sections for HRTEM were prepared by mechanical polishing and ion milling, following the procedure of Træholt et al. [9]. HRTEM imaging was performed in the electron microscope JEOL JEM-4000 EX at an acceleration voltage of 400 kV (point resolution 0.18 nm). The negatives of the micrographs obtained were converted into digital image files with a CCD camera. Computerized image processing, including careful filtering to improve image quality, was performed by help of GATAN’s Digital Micrograph 2.0 image processing software. Additionally, computer simulations of HRTEM images not shown in this paper were carried out using the MacTempas program package [10] in order to back the conclusions drawn from the HRTEM structure images. HRTEM investigations of cross-sections are suitable to reveal the interface quality and the phase composition of the bilayers. Additionally the crystallographic sites occupied by the RE cations can be determined.

2.3. Bilayers for Josephson junctions

Bilayers are the key element for the fabrication of coplanar Josephson junctions [7], whose fabrication sequence is described shortly: First a 100–200-nm thick doped bottom layer is deposited at a temperature of 860°C, covered by an 80-nm thick pure BSCCO 2212 top layer. The superconducting top layer requires a minimal oxygen flow of 10 sccm and an oxygen pressure of 2.5 mbar to achieve a typical $T_c$ of 90 K. To analyze the bilayers, among other techniques X-ray diffraction (XRD) in Bragg–Bretano geometry was used. In Fig. 1, a typical XRD
Fig. 1. X-ray diffraction pattern of a Bi$_2$Sr$_2$(Ca$_{0.8}$Gd$_{0.2}$)$_2$Cu$_2$O$_{8+δ}$ bilayer. The features indexed × and ○ represent the doped and undoped layer, respectively.

Fig. 2. (a) Cross-section of a Bi$_2$Sr$_2$(Ca$_{0.4}$Gd$_{0.6}$)$_2$Cu$_2$O$_{8+δ}$ bilayer at Scherzer focus. Black dots correspond to cation sites as marked by arrows. $N$ is the number of half unit cells stacked in [001] direction. (b) Variation of the intensity at the cation sites measured along the AB line in (a). Electron beam direction is [110].

2.4. Stabilization of the 2212 phase

This section addresses the crystallographic optimization of the 2212 films. Fig. 3 shows another part of the same Bi$_2$Sr$_2$(Ca$_{0.4}$Gd$_{0.6}$)$_2$Cu$_2$O$_{8+δ}$ Bi$_2$Sr$_2$Ca$_2$Cu$_2$O$_{8+δ}$ bilayer. This picture is taken at a defocus of −80 nm, so that the cations are imaged as bright spots. The phase intergrowth of the BSCCO structure, as described before, is clearly visible in the undoped 2212 toplayer. Besides the 2212 phase ($n = 2$) there are also $n = 3$ and 4 phases present. As a 0.6) sublayer under Scherzer focus conditions, where the cations are imaged as dark spots. The intensities measured at the cation sites are shown in Fig. 2b. They were determined from the optical density of the scanned negative at the cation positions by help of Gatan’s Digital Micrograph program package. The intensity of the Ca sites changes drastically at the interface, whereas the intensities of the Bi, Sr and Cu sites remain almost unchanged. From these results it can safely be concluded, that the Gd$^{3+}$ cations occupy Ca$^{2+}$ positions, justifying the formula Bi$_2$Sr$_2$(Ca$_{1−1}$RE$_{0.1}$)Cu$_2$O$_{8+δ}$ used in this paper. In addition the interface of the in-situ deposited bilayer is revealed to be atomically sharp.

[The rest of the text continues with detailed analysis and discussion regarding the crystallographic optimization of the 2212 phase and the implications of the experimental results.]
Fig. 3. Cross-section of a Bi$_2$Sr$_2$(Ca$_{a_x}$Gd$_{1-x}$)Cu$_2$O$_{8+y}$/Bi$_2$Sr$_2$CaCu$_2$O$_{8+y}$ interface region. \( n \) is the number of CuO-planes. The undoped upper layer includes the typical BSCCO stacking faults (marked areas). Electron beam direction is [110].

Fig. 4. Cross-section image of an optimized Bi$_2$Sr$_2$(Ca$_{a_x}$Y$_{1-x}$)Cu$_2$O$_{8+y}$ thin film consisting of the BSCCO 2212 phase only. Electron beam direction is [010].
consequence of the intermixing of the different BSCCO phases, the crystallographic structure of the superconducting toplayer reveals stacking faults. In contrast, the normal conducting doped bottom layer shows the pure 2212 phase only.

Our main goal was the stabilization of the crystallographic structure of the superconducting films by a slight doping, preserving an acceptable transition temperature. In this part of our work we concentrated on doping with the rare earth element yttrium. It turned out, that a 20% substitution of Y for Ca is sufficient to obtain a single-phase 2212 film. Fig. 4 shows a HRTEM image of the perfect crystallographic structure of such a film. In addition the superconducting behaviour was optimized by an in situ oxygen control. In comparison to the undoped 2212 films, the Y-doped films need an oxygen flow a factor five higher during deposition. As a result we are able to fabricate single phase 2212 films with a $T_c$ of 86 K, as determined by ac-susceptibility measurements.

The stabilization of the 2212 phase by RE doping is a remarkable result. In the following we present a mechanism to explain this effect. Considering the substitution of a trivalent RE ion for the twovalent Ca ion, we would like to point out the role of oxygen in charge compensation. High $T_c$ copper oxides exhibit intergrowth structures consisting of superconducting layers of a fixed oxygen concentration and ‘inactive’ layers, like the BiO layers, of variable oxygen concentration which impart anisotropy, internal electric fields and a mismatch in the bond length [11]. To get an information about the oxygenation of the BiO-slabs the behaviour of the wavelength $\lambda$ of the incommensurate modulation with respect to the kind of doping and its concentration $x$ was analyzed. The HRTEM picture in Fig. 5 shows a cross-section of the interface region of a Bi$_2$Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_{8+\delta}$ bilayer with $x = 0.2$ and $x = 0.8$, respectively. Line ABC has been drawn in such a way as to directly connect the antinodes of the wavelike contrasts of neighbouring Bi–O double.

Fig. 5. Cross-section image of a Bi$_2$Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_{8+\delta}$ bilayer with $x = 0.2$ (upper part) and $x = 0.8$ (lower part). The bright edge at the interface region is due to the preparation of the cross-section sample by ion milling. The wavelength $\lambda$ of the incommensurate modulation in the Bi–O slabs decreases with increasing doping concentration. Electron beam direction is [100].
layers. The wavelike contrasts are due to the incommensurate modulation. The change of $\Delta \alpha$ at the interface of the inclination angle $\alpha$ of this line is a measure of the change $\Delta \lambda$ of the wavelength $\lambda$ at the interface according to the following formula, which has been derived from simple geometric considerations:

$$\frac{\Delta \lambda}{\lambda} = \frac{\Delta c}{c} + 2 \frac{\Delta \alpha}{\sin 2 \alpha},$$

where $\Delta c$ is the change of the lattice parameter at the interface. As a result of our X-ray measurements $\Delta c/c = 0.09$. Furthermore, high resolution images exhibit the interface between the two films to be free from misfit dislocations, thus indicating $\Delta b/b = 0$. According to our measurements the wavelength of the incommensurate modulations amounts to $\lambda = 4.10b$ for the $x = 0.8$ bottom layer and $\lambda = 4.7b$ for the $x = 0.2$ top layer. These values are in good agreement with the results obtained by other groups [12,13]. The decrease of $\lambda$ with increasing $Y$ content [14–17] indicates the incorporation of extra oxygen in the Bi–O planes [5,13,17–19]. The increased oxygen content in the Bi–O slabs results in a charge separation, because $Y^{3+}$ and $O^{2-}$ occupy different atomic positions in the unit cell, as shown in Fig. 6. As a consequence an attractive electrostatic interaction between these ions, stabilizing the 2212 structure by a reduction of its unit cell parameter $c$, has to be considered. According to the simple electrostatic model sketched in Fig. 6, the stabilization energy is approximately $\Delta E = 0.1$ eV per substitution, assuming a dielectric constant $\varepsilon = 10$ for the Cu–O planes. If the dopant concentration $x$ is low, $\Delta E \approx 0.1x^2$ eV is a good approximation, i.e., the stabilization energy scales with the square of the doping concentration $x$. This stabilization energy is comparable with the enthalpy $\Delta H_{O^2} = 0.29$ eV/O-atom for pure BSCCO 2212 [25]. These arguments are supported by the variation of unit cell parameters $a$, $b$ and $c$ as a function of the doping concentration:

According to X-ray measurements the unit cell parameter $c$ of the 2212 phase decreases linearly with the doping concentration $x$. Since the 2212 lattice parameter is smaller than the 2223 lattice

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**Fig. 6.** Model of the $Y^{3+}$ substitution for $Ca^{2+}$ occurring in the 2212 and 2223 structures. $c$ is the unit cell parameter of 2212 ($c = 3.089$ nm), $+e$ and $-e$ indicate an excess of electrostatic charge due to $Y^{3+}$ and $O^{2-}$, respectively.
parameter, this tendency obviously ends in the 2212 phase. The decrease of \( c \) was found also in different structural analyses of corresponding single crystals and polycrystalline BSCCO [8,12–17]. Quitmann et al. [8] and Calestani et al. [12] observe this decrease to be accompanied by a complementary increase of the unit cell parameters \( a \) and \( b \), although the ionic radius of \( Y^{3+} \) is approximately 10% smaller compared to \( Ca^{2+} \). Obviously the attractive electrostatic interaction between the positively charged \( Y^{3+} \) and the negatively charged oxygen \( O^{2-} \) ions results in a compression of the \( Cu-O \) and \( Sr-O \) atomic layers along the \( c \) direction and consequently in an increase of the lattice parameters \( a \) and \( b \).

In the reverse case, substituting \( Pb^{2+} \) for \( Bi^{3+} \), \( \lambda \) increases with the \( Pb \) concentration [20,22,23]. Referring to Green et al. [24], \( Pb \) doping stabilizes the 2223 structure and the 2223 phase can only be formed, if neighbouring (\( Bi \), \( Pb \))–\( O \) slabs are ‘properly’ oxygenated. The stabilization of the 2223 structure by the substitution of divalent \( Pb \) for trivalent \( Bi \) and the increase in \( \lambda \) imply, that the ‘proper’ amount of oxygen is lower than in unstabilized \( Pb \)-free structures. In addition a \( 2^+ \rightarrow 3^+ \) doping removes the common 2201 stacking faults [21] from 2212 single crystals [20]. In other words, a \( 2^+ \rightarrow 3^+ \) substitution stabilizes BSCCO phases with larger \( c \)-axis parameters, whereas in this paper we presented the stabilization of a BSCCO phase with a smaller \( c \)-axis parameter by a \( 3^+ \rightarrow 2^+ \) doping. Both kinds of stabilization are based on the simple electrostatic model proposed here.

3. Conclusions

Superconducting–normalconducting multilayers were deposited by an in-situ DC-sputter technique using differently doped \( Bi_{1-x}Sr_x(Ca_{1-y}RE_y)Cu_2O_{2+y} \) layers. HRTEM analyses of the multilayers revealed perfect interfaces. A significant improvement of the crystallographic quality of the normalconducting layers was achieved by RE doping. The crystallographic structure of the superconducting thin films was optimized by a slight doping of yttrium for calcium, preserving a \( T_c \) of 86 K. HRTEM pictures of 20% \( Y \) doped films show a crystallographic structure of high quality, consisting of the 2212 phase only. This monophasic stability is explained by an electrostatic model, which is supported by measurements of the \( c \)-axis parameter and the wavelength \( \lambda \) of the incommensurate modulation in the \( Bi–O \) slabs as a function of doping concentration \( x \).

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